Palladium Complexes Containing Potentially Chelating Pyridylidene-Type Carbene Ligands

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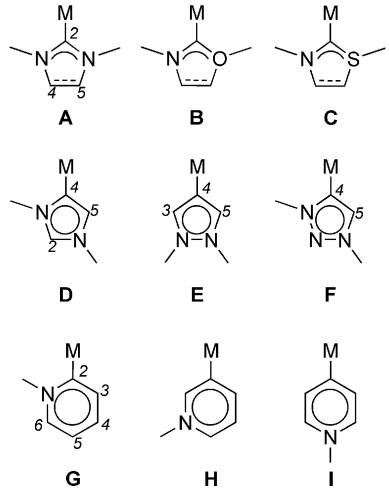
Oxidative addition of 2-bromopyridine derivatives containing a potentially chelating donor group E (E = NMe_2, SMe, SPh) to palladium(0) gives *C,E*-bound pyridylpalladium(II) complexes. Mono-, di-, and polymeric palladium complexes are obtained depending on the type of functionalization at the pyridyl nitrogen. With a lone pair at nitrogen, dimetallic products are isolated, while protonation gives monometallic pyridylidene-type complexes. Remarkably, *N*-methylation inhibits chelating ligand coordination and a one-dimensional polymer is formed instead. Heck-type arylation of styrene is used as a probe for the catalytic activity of the palladium pyridylidene complexes and reveals moderate activities. Mechanistic studies support a heterogeneous mode of action, including loss of the pyridylidene-type ligand from the metal coordination sphere.

Introduction

The application of *N*-heterocyclic carbenes (NHCs) as ligands for transition metals has thus far focused largely on 2-imidazolylidenes and the corresponding *O*- and *S*-derivatives (oxazolylidenes and thiazolylidenes, respectively), and their C–C saturated congeners (**A**–**C**, Scheme 1).[1] NHCs that lack such extensive heteroatom stabilization of the metal-bound carbon are less studied, perhaps because the free carbene is less easily accessible.[2] Despite the pioneering work of Bertrand and co-workers,[3] who elegantly demonstrated that low heteroatom stabilization does not preclude the formation of stable free carbenes, protocols for the metalation of less heteroatom-stabilized carbene ligand precursors often avoid the formation of free carbenes. We[4] and others[5] have recently synthesized a variety of abnormal and remote carbene complexes that contain NHC ligands with heteroatoms positioned remote from the carbene-type carbon in reactions based, for example, on oxidative addition, direct C–H bond activation (including cyclometalation), or transmetalation (see **D**–**I** in Scheme 1 for examples).

Pyridylidene-type systems (**G**–**I** in Scheme 1) are a particularly attractive subclass of NHC ligands since pyridine functionalization is highly versatile.[6] In addition, recent work by Raubenheimer and Herrmann has demonstrated the utility of pyridylidene complexes for catalysis.[7] Pyridylidene complexes have become accessible by a variety of methods, predominantly[8] C–H bond activation,[9] pyridyl alkylation,[10] and oxidative addition.[11]



Scheme 1. Different types of carbene ligands bound to transition metals.

We became interested in combining the synthetic versatility of pyridine chemistry and the catalytic activity of pyridylidene-type complexes and report here on the impact of pyridylidene ligands that incorporate chelating donor sites. Special attention has been paid to investigating the properties and catalytic activity of the coordinated metal center as a consequence of using different (potentially permanent and labile) groups for nitrogen quaternization, in other words for inducing pyridylidene-type ligand bonding.

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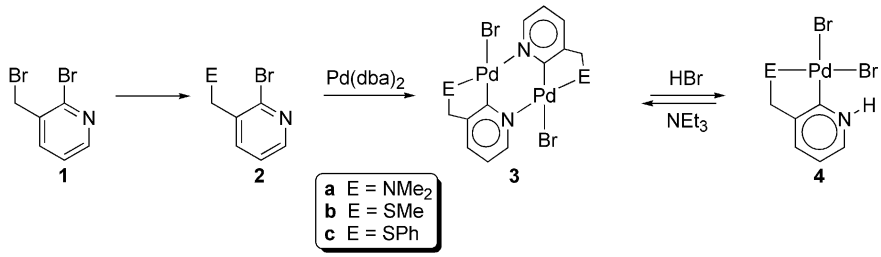


Scheme 2. Synthesis of palladium pyridylidene complexes by a metalation–quaternization sequence (route B).

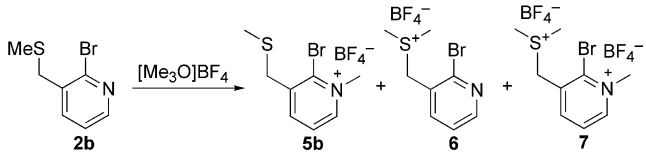
Results and Discussion

Synthesis of Complexes

Previously reported syntheses of chelating pyridylidene complexes generally involve C–H bond activation strategies,[9b–9f] although the heteroatom assistance in this process may be different from that of a classical cyclometalation.[12] In this work, we have chosen an oxidative addition protocol in order to direct metalation selectively towards the pyridine 2-position. Thus, functionalization of the *meta* position of 2-bromopyridine according to known procedures[13] afforded 2-bromo-3-(bromomethyl)pyridine (**1**; Scheme 2).

Subsequent nucleophilic substitution with different donor groups yielded the ligand precursors **2a**–**c**, which contain a hard and basic NMe_2 functionality (**2a**), a softer SMe group (**2b**), or a mildly basic and potentially weakly coordinating SPh donor site (**2c**) as donor group. Two conceptually different routes then exist for the fabrication of pyridylidene-metal complexes. First, and analogous to classical imidazolium-derived NHC chemistry,[1] the pyridine heterocycle can be transformed into the pyridinium salt by nitrogen quaternization and subsequently be metalated (route A). Alternatively, metalation of the pyridine may occur prior to *N*-functionalization (route B). With ligands **2a**–**c**, nitrogen alkylation (i.e., route A) appeared to be delicately balanced by the basicity of the heteroatom in the donor group on one hand and by the stereoelectronic effects exerted by the bromide in the *ortho* position of the pyridine nitrogen on the other. Generally, the alkylation selectivity was low for **2a** and **2b**. For example, a mixture containing the pyridinium and sulfonium salts **5b** and **6**, respectively, was obtained in an approximate 4:3 ratio, along with some dicationic species **7**, when using one molar equivalent of $[Me_3O]BF_4$ for the alkylation of **2b** (Scheme 3). The alkylation chemoselectivity appeared to be virtually independent of the reaction conditions (MeI in THF, MeI in AcOH, $[Me_3O]BF_4$ in CH_2Cl_2/MeCN). In contrast, alkylation of **2c** proceeded smoothly due to the low nucleophilicity of the phenyl-substituted sulfur, and the corresponding pyridinium salt **5c** was obtained in good yields (see below).

As a consequence of the low chemoselectivity of alkylation, route B, which involves a metal insertion–quaternization sequence, was further pursued for the synthesis of pyridylidene complexes. Thus, oxidative addition of ligands **2a**–**c** to $[Pd(dba)_2]$ provided the dimeric complexes **3a**–**c** as



Scheme 3. Product mixtures obtained upon alkylation of **2b**.

yellow solids (Scheme 2). Similar pyridine-bridged rather than halide-bridged dimeric structures have been observed previously.[14] Complexes **3a**–**c** are soluble in chlorinated solvents and in polar media such as MeCN and DMSO. Crystal structure determinations of **3a** and **3b** unambiguously confirmed their dimeric structure (Figure 1). Both complexes are characterized by a central six-membered dipalladacycle in a boat-type conformation containing the

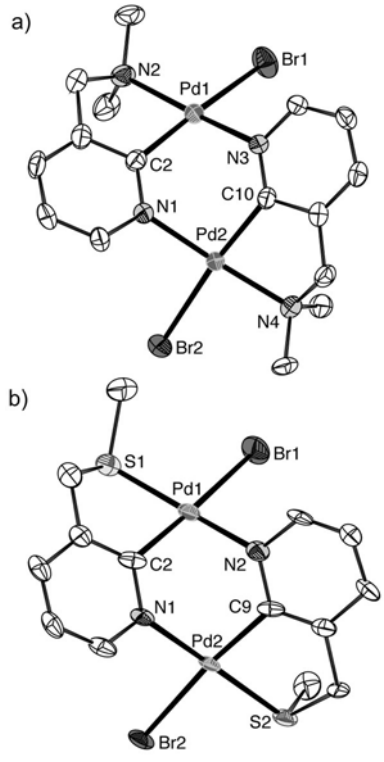


Figure 1. ORTEP representation of the molecular structures of complexes **3a** (a) and **3b** (b) (50% probability ellipsoids; hydrogen atoms, co-crystallized solvent molecules, and the second crystallographically independent molecule in the asymmetric unit of **3b** have been omitted for clarity).

two palladium centers and the metal-bound carbons and pyridine nitrogens. Additionally, two metallacycles are formed due to the *E*,*C*-bidentate coordination of the ligand. These metallacycles are puckered, with the palladium square plane being twisted with respect to the heterocyclic pyridyl plane. The geometry around the two metal centers in each structure is identical, albeit not crystallographically. The palladium–carbon bond lengths range from 1.951(5) to 2.002(13) Å (Table 1) and do not indicate a pronounced double bond character due to carbene-like bonding. Carbenoid bonding may be surmised if the metal center is considered as a (weakly) quaternizing group at nitrogen. The ligand bite angles in both complexes **3a** and **3b** are identical (angle C–Pd–E: 82.1°). The crystals of **3b** contain two crystallographically independent complex molecules with the two sulfur atoms in each molecule in opposite configurations, thus providing a racemic mixture of [PdBr(pyridylidene)] units.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **3a** and **3b**.

	3a		**3b**
Pd1–C2	1.951(5)	Pd1–C2	1.972(14)
Pd2–C10	1.959(5)	Pd2–C9	2.002(13)
Pd1–N2	2.082(4)	Pd1–S1	2.274(4)
Pd2–N4	2.091(4)	Pd2–S2	2.265(4)
Pd1–N3	2.045(4)	Pd1–N2	2.044(11)
Pd2–N1	2.047(4)	Pd2–N1	2.087(11)
Pd1–Br1	2.5560(6)	Pd1–Br1	2.5336(19)
Pd2–Br2	2.5485(6)	Pd2–Br2	2.5380(15)
C2–Pd1–Br1	169.22(13)	C2–Pd1–Br1	174.6(4)
C2–Pd1–N2	82.14(18)	C2–Pd1–S1	82.1(4)
C2–Pd1–N3	94.00(17)	C2–Pd1–N2	93.2(5)
N2–Pd1–N3	169.58(15)	S1–Pd1–N2	170.4(3)
N2–Pd1–Br1	94.37(12)	S1–Pd1–Br1	93.78(11)
N3–Pd1–Br1	91.09(10)	N2–Pd1–Br1	91.4(3)

The ^{1}H NMR spectra of the complexes (DMSO solutions) feature broad resonances, which may be rationalized by a conservation of the dimeric structure in solution. Specifically, the signal assigned to the nitrogen-bound CH_2 group in **3a** appears as a broad singlet at δ_H = 4.13 ppm (50 °C, DMSO solution), with a decoalescence temperature close to room temperature. In CD_2Cl_2 solution, the AB signal ($^2J_{H,H}$ = 14.3 Hz) is well resolved at temperatures below –10 °C and coalescence occurs at around room temperature. This fluxional behavior presumably reflects the slow puckering of the five-membered N–C–C–C–Pd palladacycle. While this process is generally fast on the NMR timescale in related metallacycles (see below),[15] a substantial deceleration is expected in the dimeric structure because of pyridine coordination. As a consequence, puckering of one metallacycle is concerted with the puckering of the other five-membered palladacycle and includes inversion of the boat conformation of the central dimetallacycle. Based on the resonance separation, an activation energy, $\Delta G^{\ddagger}$, of 54.6(±1.0) kJ mol^{-1} was calculated for the puckering process in **3a**.

The CH_2 group in the sulfur-containing complex **3b** appears as two sets of broad AB signals at room temperature, which coalesce at elevated temperatures [T_{coal} = 323 K, $\Delta G^{\ddagger} \approx 63(\pm 2)$ kJ mol^{-1}]. The AB patterns are well distinguishable in CD_2Cl_2 solution at –20 °C and reveal two isomers due to the presence of two AB patterns ($^2J_{H,H}$ = 15.9 and 13.1 Hz). The low-field part of each AB set is further split into a doublet of doublets, probably because of the favorable dihedral angle between the pyridine H4 and the equatorial proton of the methylene group. At the slow-exchange limit, rigid coordination of the sulfur donor to palladium creates a new center of chirality and renders the methylene protons diastereotopic (cf. crystal structure of **3b** above). Intriguingly, coalescence of all methylene signals of **3b** is simultaneous, thereby suggesting that inversion of the configuration at sulfur is mechanistically associated with the puckering process. Accordingly, transient Pd–S dissociation may rationalize the fluxional behavior. Such a model is further supported by the lower coalescence temperature in DMSO as compared to CD_2Cl_2 solutions. The CH_2 group in complex **3c** appears as a doublet located at δ_H = 4.14 and 5.03 ppm, respectively (500 MHz, DMSO solution). No coalescence was observed for **3c** up to 343 K, thus suggesting an activation energy of more than 65 kJ mol^{-1}.

Successful cleavage of the dimers was accomplished with methanolic HBr and produced the monometallic pyridylidene complexes **4a**–**c**. An excess of HBr may be used without affecting the Pd–$C_{pyridylidene}$ bond, thus suggesting a pronounced stability of this bond. In contrast, scission of the Pd–N bond of **4a** was noted under these strongly acidic conditions. Addition of a base such as NEt_3 to the pyridylidene complexes **4a**–**c** regenerated the dimeric complexes **3a**–**c**. Formation of the monomeric complexes **4a**–**c** was suggested by the sharp ^{1}H NMR resonances. Obviously, ring puckering in the monometallic complexes is fast on the NMR time scale. Most intriguingly, the methylene protons of **4b** and **4c** appear as singlets at δ_H = 4.43 and 4.81 ppm, respectively, thus indicating a rapid inversion of the configuration at sulfur as well. Accelerated inversion rates may be a consequence of the higher *trans* effect of bromide in **4** as compared to pyridine in **3**.

All three pyridylidene complexes **4a**–**c** were characterized by single-crystal X-ray diffraction. Their molecular structures are shown in Figure 2, and pertinent bond lengths and angles are collected in Table 2. Crystals of **4b** contain two crystallographically independent molecules in the unit cell, with the methyl substituent in a pseudo-axial position [dihedral angle C2–Pd1–S1–C7 84.4(6)°] in both molecules. In contrast, the sulfur substituent in **4c** is in a pseudo-equatorial orientation. Both complexes **4b** and **4c** crystallize as racemates in the centrosymmetric space group $P2_1/n$. The global features of all three structures **4a**–**c** are very similar. The palladium square-plane is distorted and features Pd1–Br2 bonds that are consistently longer than the Pd1–Br1 distances. This result is in good agreement with a higher *trans* influence of the pyridylidene carbon as compared to the heteroatom donor. The Pd–Br1 bond length seems to reflect the quality of the donor and is largest for soft and

basic SMe, decreases upon reduction of the sulfur basicity (SPh), and is smallest opposite the hard-soft most-mismatched Pd–NMe_2 bond. The Pd–$C_{pyridylidene}$ bond is shorter in **4a** than in **4b** and **4c**, which is presumably a direct consequence of the size of the metallacycle. The cycle in **4a** is comparably small due to the presence of nitrogen, while it is more expanded with sulfur. Similar differences may be pointed out when comparing the structures of **3a** and **3b** (see above). Intramolecular N–H_N···Br1 hydrogen bonding was found to provide additional stability in all structures **4a**–**c**. While the nitrogen-bound hydrogen atom was introduced at calculated positions (N–H_N 0.88 Å) in **4a** and **4b**, it was located in the Fourier difference map in **4c** [N–H_N 0.86(4) Å]. This bonding closes a second metallacycle in the complexes and provides an overall structure reminiscent of pincer-type complexes.[16] The short H···Br contacts are presumably a consequence of the acidity of the nitrogen-bound proton paired with the steric constraints imposed by the chelating bonding mode of the pyridylidene ligand, which predisposes the metal-bound bromide and the hydrogen in close proximity.[17] No such hydrogen bonding has been observed in related palladium(II) complexes with *C*,*N*- or *C*,*S*-bidentate ligands comprising a phenyl instead of a pyridylidene as the *C*-donor unit, despite similar torsion angles between the metal coordination plane and the aryl ligand [average dihedral angle of all structures **4a**–**c** is 12(4)°].[18]

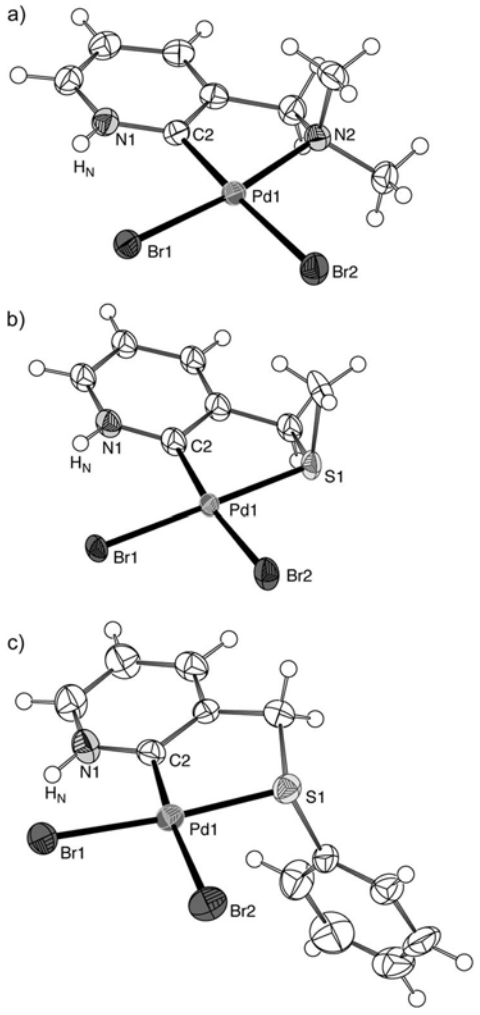


Figure 2. ORTEP representation of the molecular structures of complexes **4a** (a), **4b** (b), and **4c** (c) (50% probability ellipsoids; the second crystallographically independent molecule in the asymmetric unit of **4b** has been omitted for clarity).

Table 2. Selected bond lengths [Å] and angles [°] for complexes **4a**–**c**.

	4a (E = N2)	**4b** (E = S1)	**4c** (E = S1)
Pd1–C2	1.960(2)	1.974 (11)	1.981(5)
Pd1–E	2.094(2)	2.260 (2)	2.2648(12)
Pd1–Br1	2.4232(3)	2.4662(11)	2.4375(7)
Pd1–Br2	2.5173(4)	2.4908(13)	2.4958(8)
N1···Br1	3.174(2)	3.199(9)	3.140(4)
H_N···Br1	2.58	2.57	2.54(4)
C2–Pd1–E	81.66(10)	84.9(3)	85.23(13)
C2–Pd1–Br1	91.82(7)	93.3(3)	92.63(12)
C2–Pd1–Br2	176.25(7)	177.84(8)	172.99(12)
E–Pd1–Br1	172.54(6)	172.1(3)	175.22(4)
E–Pd1–Br2	94.66(6)	93.53(4)	88.95(4)
Br1–Pd1–Br2	91.893(11)	93.53(4)	93.47(3)
N1–H_N···Br1	126	130	128(3)
Br1–Pd1–C2–N1	8.9(2)	16.0(9)	12.7(4)
E–Pd1–C2–C3	12.4(2)	8.5(9)	6.4(3)

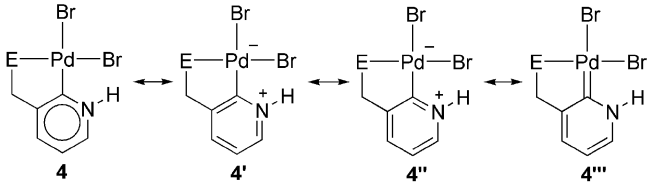
The Pd–C bond lengths are similar to those in related complexes containing bidentate arylamine or chelating NHC ligands.[19] No compelling evidence is thus found for a carbene-type Pd=C double bond based on the bonding situation around the metal center. Inspection of the bond lengths in the heterocycle was more instructive, in particular when comparing the C–C distances (Table 3). All C–C bonds in the structure of **4a** are similarly long and suggest a double bond delocalization (cf. resonance structures **4′** and **4′′** in Scheme 4). Conversely, slight bond alternation is noted in complex **4c**, with shorter C3–C4 and C5–C6 bonds pointing to partially localized double bonds and a more substantial contribution of resonance structure **4′′′**. The differences are relatively small, however, and are often within the 3σ significance range. This is probably best illustrated when comparing the two molecules in the asymmetric unit of complex **4b**. Thus, while pyridylidene resonance structure **4b′′′** is supported by the C–C bond length alternation and also by the relatively short Pd–C distance in molecule 1, molecule 2 reveals rather delocalized double bonds and features a comparably long Pd–C bond, in line with a zwitterionic structure **4b′**/**4b′′**. Similarly, the hydrogen bonding in molecule 1 is slightly stronger than in mole-

Table 3. Selected heterocyclic bond lengths [Å] for complexes **4a**–**c**.

	4a	**4b** molecule 1	**4b** molecule 2[a]	**4c**
C2–C3	1.397(4)	1.420(14)	1.437(14)	1.399(6)
C3–C4	1.387(4)	1.362(16)	1.358 (13)	1.379(7)
C4–C5	1.388(4)	1.397(14)	1.377(14)	1.392(8)
C5–C6	1.366(4)	1.364(14)	1.391(13)	1.352(8)
Pd1–C2	1.960(6)	1.974(11)	2.002(9)	1.981(5)
Pd1–Br2	2.5173(4)	2.4908(13)	2.4997(12)	2.4958(8)

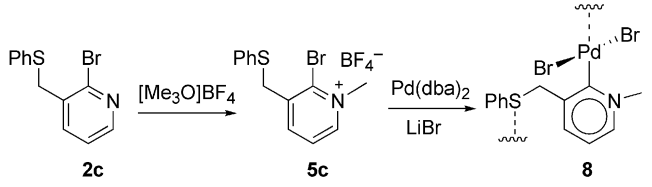
[a] Atom labeling adapted.

cule 2 (H_N···Br1 = 2.55 and 2.57 Å, respectively), which is in line with a more acidic proton and a higher iminium character of nitrogen. Obviously, chemical differentiation (e.g., due to different substitution patterns, variation in donor properties, chelate size) cannot account for the observed structural changes. Accordingly, the limiting zwitterionic structures **4′** and **4′′**, and the neutral pyridylidene resonance form **4′′′**, should be very close in energy and are probably indistinguishable in solution.



Scheme 4. Resonance structures contributing to pyridylidene complexes, featuring charge delocalization (**4**), charge localization in zwitterionic species (**4′** and **4′′**), and double bond localization in a carbene-type species (**4′′′**).

Alkylation rather than protonation of the pyridine nitrogen in the dimeric complexes **3a**–**c** using MeI, MeOTf, or $[Me_3O]BF_4$ has been unsuccessful thus far. Apparently, dissociation of the Pd–N_{pyr} bond in **3** is disfavored. As the pyridinium ligand precursor **5c** was readily available, oxidative addition afforded the pyridylidene complex **8** (Scheme 5) by initial alkylation and subsequent metalation (route A), as opposed to the sequence used for complexes **4a**–**c**. The spectroscopic data of this complex are slightly different from those of **4c**. Thus, the CH_2 protons appear at lower field (δ_H = 5.02 in **8** and 4.78 ppm in **4c**) and the carbon signal of this group is at significantly higher field (δ_C = 37.7 in **8** vs. 46.1 ppm in **4c**). While these data are in agreement with sulfur coordination to the metal center, they suggest different coordination modes in **4** and **8**.



Scheme 5. Synthesis of the polymeric pyridylidene complex **8**.

In the solid state, complex **8** was found to be a one-dimensional polymer consisting of palladium centers interlinked by a bridging κ^2-*C*,*S*-coordinating pyridylidene ligand (Figure 3). Obviously, alteration of the nitrogen substituent from a proton (as in **4c**, cf. Figure 2, c) to a methyl group disfavors chelation, presumably because of steric repulsion between the metal-bound bromide and the *N*-bound methyl group. In coordination complexes, such repulsion is known to be relieved by a strongly distorted ligand arrangement around the palladium center.[20] Chelation of the pyridylidene ligand in **8** would induce a small torsion angle between the metal square plane and the aryl ring. In the bridging coordination mode, however, this torsion angle is maximized [angle Br1–Pd1–C2a–N1a: 91.8(7)°], which means that the *N*-bound methyl group resides above the metal coordination plane and may be involved in stabilizing H···Pd interactions. Short contacts were also observed between one of the *ortho* hydrogens of the SPh unit and palladium (H13···Pd1 2.72 Å). The pyridylidene and sulfur donor sites are in mutual *trans* positions [angle C2a–Pd1–S1: 174.4(3)°]. The Pd1–C2a bond length is 1.966(9) Å and hence at the shorter edge for an unsupported Pd–C(sp^2) single bond.[5q] Notably, no bond alternation was observed in the pyridylidene heterocycle to support a double bond-localized resonance structure similar to **4′′′** (cf. Scheme 4).

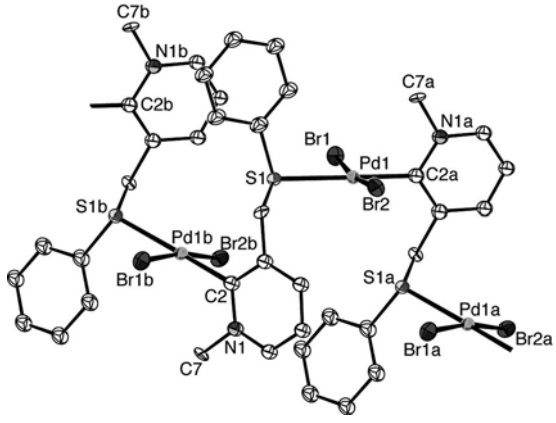


Figure 3. ORTEP representation of the polymeric structures of **8** (50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–C2a 1.966(9), Pd1–S1 2.412(2), Pd1–Br1 2.4342(12), Pd1–Br2 2.4410(11); C2a–Pd1–S1 174.4(3), C2a–Pd1–Br1 87.2(3), C2a–Pd1–Br2 89.3(3), S1–Pd1–Br1 87.29(6), S1–Pd1–Br2 96.28(6), Br1–Pd1–Br2 171.26(4).

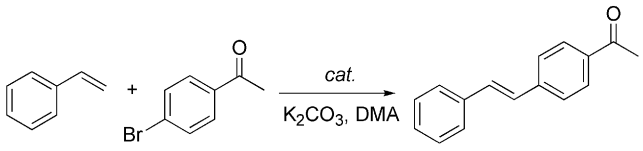
NMR Spectroscopic Analyses

Spectroscopic analyses were performed in order to evaluate the effect of different functional groups at the pyridine nitrogen, namely an alkyl group (CH_3 in **8**), a proton in **4**, and a PdL_3 fragment in **3**. Comparison of the ^{1}H NMR resonances provided little insight.[21] The signals due to the metal-bound carbons appear in the ^{13}C NMR spectrum at around δ_C = 180 (for **3**), 174 (for **8**), and 171 ppm (for **4**). These resonance frequencies compare well with those of related pyridylidene-palladium complexes but are clearly at higher field than the carbene in the pyridylidene-platinum complex reported by Rourke and co-workers.[9a] The observed trend may reflect the inductive effect exerted by the adjacent nitrogen nucleus rather than a modification of the metal–carbene bonding. Such a conclusion is supported by the chemical shift differences of C6 (δ_C = 151 in **3**, 143 in **8**, and 140 ppm in **4**), which are strongly related to those of the metal-bound C2 nucleus. The negative inductive effect of nitrogen is expected to become weaker with increasing donor ability of the quaternizing functional group, that is,

$N–PdL_3 > N–H > N–CH_3$. The observed inversion of N–H and $N–CH_3$ in this sequence may be a consequence of the hydrogen bonding in **4**.

Catalysis

The impact of pyridylidene-type ligands on the catalytic activity of the coordinated palladium center was probed in the Mizoroki–Heck reaction. The arylation of styrene with bromoacetophenone in *N*,*N*-dimethylacetamide (DMA) was used as a model reaction (Scheme 6).



Scheme 6. Mizoroki–Heck reaction employed for catalyst testing.

Due to the basic conditions used for Mizoroki–Heck reactions, combined with the fact that bases induce rapid transformation of complexes **4a**–**c** into their corresponding dimers **3a**–**c**, catalyst screening focused on complexes **3a**–**c** and **8** and their solvent analogs. Initial runs indicated full conversion after approximately 4 h when activated aryl bromides were used as substrates (Table 4, entries 1–4). No conversion was observed with aryl chlorides,[22] even after prolonged reaction times. These results compare well with the catalytic activity of related chelating pyridylidene-palladium complexes.[23] Only small differences were noted upon variation of the donor group E in the dimeric catalyst precursors **3a**–**c**. Similarly, conversions with complex **8** did not markedly differ from those obtained with the dimeric complexes **3a**–**c** (Table 4, entry 4). Abstraction of the metal-bound halides and starting from the solvent complexes of **3** or **8** enhanced the initial turnover frequencies slightly (cf. conversions after 20 min for entries 5–8, Table 4), although the catalytic performance levels off to the activity of the parent bromo complexes after this time.

High reaction temperatures are required for efficient catalysis. At 100 °C, catalyst **3a** gave only 56% conversion after 24 h, and no conversion at all was observed within this time frame at 70 °C (Table 4, entries 9, 10). The need for high temperatures, even for converting activated aryl bromides, suggests that the catalysts operate heterogeneously.[24] The similar activities of all complexes further strengthens this hypothesis. Moreover, higher catalyst loadings (>5 mol-%) did not give faster conversions than the 0.2 mol-% used in the initial runs (Table 4, entries 11, 12). No induction time was observed when using catalyst **8**, while the catalytic activity of **3a** only begins after around 10 min (Figure 4). The induction period for complex **3a** may be required for dissociation of the donor group E, a process that has been assumed to be essential for Heck catalysis using related pincer-type palladium complexes.[25] Obviously, this step is redundant when using catalyst precursor **8**. The kinetics of the reaction are, however, not sigmoidal but rather characteristic of homogeneous catalysis. Poisoning experiments using PPh_3 were not conclusive, since the activity of the catalyst was not influenced upon addition of 0.3 or 3 mol equiv. of phosphane. It should be noted, however, that the catalytic system is highly sensitive to the presence of mercury, with substrate consumption essentially ceasing upon addition of excess Hg^0 to an active catalytic mixture (Table 4, entries 13, 14). This result lends further support to a heterogeneous working mode of these palladium pyridylidene systems.[26] Accordingly, palladium reduction and dissociation of the pyridylidene-type ligand constitutes a key step in entering the catalytic cycle with complexes **3** and **8**. Metal reduction to palladium(0) may be more facile in the monomeric complex **8** than in the dimers **3a**–**c**, perhaps because the ligand in complex **8** contains a methylated nitrogen, which ensures a more pronounced pyridylidene-type ligand bonding mode. A similar rationale may account for the higher catalytic efficiency of the solvent complex of **8** with respect to the dibromide.

Table 4. Catalytic activity of palladium complexes **3**, **8** and their solvent homologs in the Mizoroki–Heck arylation of styrene (Scheme 6).[a]

Entry	Cat.	*T* [°C]	$Conv._{20}$[b]	$Conv._{2h}$[b]	$Conv._{6h}$[b]
1	**3a**	140	13	64	97
2	**3b**	140	29	86	96
3	**3c**	140	32	87	95
4	**8**	140	25	71	98
5	**3a**[c]	140	21	64	98
6	**3b**[c]	140	36	90	95
7	**3c**[c]	140	22	70	98
8	**8**[c]	140	36	79	97
9	**3a**	100	2	3	56[d]
10	**3a**[c]	70	0	0	0
11	**3a**[c,e]	140	12	68	96
12	**8**[e]	140	23	45	93
13	**3a**[f]	140	19	19	20
14	**8**[f]	140	34	39	40

[a] General conditions: aryl bromide (1 mmol), styrene (1.5 mmol), K_2CO_3 (1.1 mmol), catalyst (2 μmol, 0.2 mol-%), DMA (5 mL). [b] Conversions after 20 min ($conv._{20}$), 2 h ($conv._{2h}$), and 6 h ($conv._{6h}$). [c] Catalyst precursor treated with 2 mol equiv. of $AgBF_4$ prior to catalytic run. [d] Conversion after 24 h. [e] 8 mol-% catalyst. [f] Addition of Hg^0 (3.0 g, 15 mmol) 20 min after initiating the reaction.

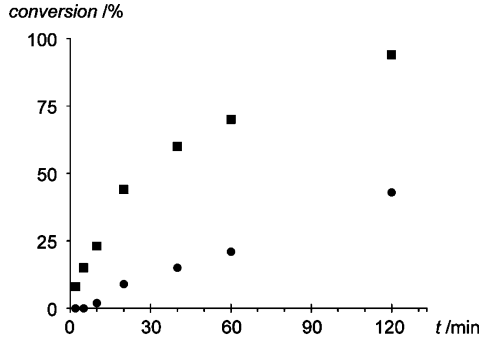


Figure 4. Time-dependent profile of the arylation of styrene catalyzed by **3a** (circles) and **8** (squares).

Conclusions

A series of palladium(II) complexes containing a chelating 2-pyridylidene type ligand has been prepared. The pyridine nitrogen was quaternized with a PdL_3 fragment, a proton, or an alkyl group. These different quaternizations alter the electronic properties at the nitrogen atom and, indirectly, also at the palladium center. Specifically, methylation of the pyridine nitrogen prevents the formation of chelating 2-pyridylidene complexes due to steric constraints between the *N*-methyl group and the ligand *trans* to the chelating donor site. Heck-type arylation of styrene appears to be slightly faster with monodentate pyridylidenes containing an alkylated rather than metalated pyridine nitrogen. The achieved conversions suggest that thioethers do not poison the catalytic activity of the palladium center. Further, mechanistic studies support a heterogeneous mode of action for this catalytic reaction. In our work, kinetic plots erroneously support a seemingly homogeneous reaction and it is obviously safer to rely on multiple mechanistic probes than on kinetic analyses alone. The prime function of the pyridylidene ligand in the palladium complexes studied here seems to consist of releasing the metal center, perhaps via reductive elimination. Such effects may need to be taken into consideration in attempts to improve the catalytic performance of these and related palladium pyridylidene complexes.

Experimental Section

General: Air-sensitive reactions were carried out under Ar using Schlenk techniques. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), tetrahydrofuran (THF) and CH_2Cl_2 were dried by passage through solvent purification columns. 2-Bromo-3-(bromomethyl)pyridine was prepared according to literature procedures.[13] All other chemicals are commercially available and were used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with Bruker spectrometers at room temperature, unless stated otherwise, and were referenced to external $SiMe_4$. Chemical shifts (δ) are given in ppm; coupling constants J are given in Hz. Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift correlation spectroscopy. Elemental analysis were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany) and of the ETH Zürich (Switzerland).

Synthesis of 2a: $HNMe_2$ (20 mL, 300 mmol) was added to an ice-cold solution of **1** (1.509 g, 6.01 mmol) in dry THF (25 mL) and the mixture stirred under Ar for 16 h. After addition of H_2O (70 mL), the pH of the mixture was adjusted to above 11 by addition of saturated aqueous K_2CO_3 and the solution was extracted with Et_2O (3 × 70 mL). The combined organic phases were washed with H_2O/brine, dried with Na_2SO_4, and evaporated to give **2a** as a yellow oil (0.982 g, 76%). A microanalytically pure sample was obtained upon recrystallization of the corresponding HCl salt **2a**·2 HCl from MeOH/Et_2O. ^1H NMR (360 MHz, $CDCl_3$): δ = 8.26 (dd, $^3J_{H,H}$ = 4.6, $^4J_{H,H}$ = 1.7 Hz, 1 H, H^6_{pyr}), 7.77 (dd, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.7 Hz, 1 H, H^4_{pyr}), 7.27 (dd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 4.6 Hz, 1 H, H^5_{pyr}), 3.51 (s, 2 H, CH_2), 2.31 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$): δ = 148.2 (C^6_{pyr}), 143.8 (C-Br), 138.7 (C^4_{pyr}), 135.5 (C^3_{pyr}), 122.7 (C^5_{pyr}), 62.0 (CH_2), 45.4 (CH_3) ppm. $C_8H_{13}BrCl_2N_2$ (288.01): calcd. C 33.36, H 4.55, N 9.73; found C 33.41, H 4.63, N 9.88.

Synthesis of 2b: Solid $NaSCH_3$ (0.660 g, 9.4 mmol) was added to a solution of **1** (2.081 g, 8.3 mmol) in dry THF (20 mL) and the mixture was stirred under Ar for 16 h. After addition of H_2O (80 mL), the pH of the reaction mixture was adjusted to above 11 by addition of saturated aqueous K_2CO_3. The solution was extracted with Et_2O (3 × 80 mL). The combined organic phases were washed with H_2O/brine, dried with Na_2SO_4, and the solvents evaporated to dryness to yield **2b** as a yellow oil (1.465 g, 81%). ^1H NMR (360 MHz, $CDCl_3$): δ = 8.25 (dd, $^3J_{H,H}$ = 4.8, $^4J_{H,H}$ = 1.8 Hz, 1 H, H^6_{pyr}), 7.68 (dd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.8 Hz, 1 H, H^4_{pyr}), 7.25 (dd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 4.8 Hz, 1 H, H^5_{pyr}), 3.76 (s, 2 H, CH_2), 2.05 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$): δ = 148.2 (C^6_{pyr}), 144.0 (C-Br), 138.5 (C^4_{pyr}), 135.1 (C^3_{pyr}), 122.7 (C^5_{pyr}), 37.3 (CH_2), 15.2 (CH_3) ppm. C_7H_8BrNS (218.11): calcd. C 38.55, H 3.70, N 6.42; found C 38.62, H 3.76, N 6.36.

Synthesis of 2c: A solution of BuLi (5 mL, 1.6 M in hexane, 8 mmol) was added dropwise to a solution of PhSH (1 mL, 9.8 mmol) in dry THF (20 mL) at –78 °C. The solution was stirred at low temperature for 2 h before adding a solution of **1** (2.0 g, 8 mmol) in dry THF (3 mL). The mixture was stirred at –78 °C for a further hour and then left to warm to room temp. After 16 h, H_2O (60 mL) was added and the pH was adjusted to above 11 with saturated aqueous K_2CO_3. The mixture was extracted with Et_2O (3 × 60 mL) and the combined organic layers were washed with H_2O/brine and dried with Na_2SO_4. Evaporation of all volatiles afforded **2c** as a yellow oil (1.944 g, 87%). ^1H NMR (360 MHz, $CDCl_3$): δ = 8.23 (dd, $^3J_{H,H}$ = 4.7, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^6_{pyr}), 7.50 (dd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^4_{pyr}), 7.35–7.21 (m, 5 H, H_{Ph}), 7.14 (dd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 4.7 Hz, 1 H, H^5_{pyr}), 4.14 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$): δ = 148.4 (C^6_{pyr}), 144.0 (C-Br), 138.4 (C^4_{pyr}), 134.5 (C^3_{pyr}), 134.5 (C_{Ph}), 130.8 (C_{Ph}-H), 129.0 (C_{Ph}-H), 127.1 (C_{Ph}-H), 122.7 (C^5_{pyr}), 39.0 (CH_2) ppm. HR-MS (ESI): *m*/*z* 279.97977 and 281.97717 (calcd. 279.97901 for $C_{12}H_{11}{}^{79}BrNS^+$ and 281.97696 for $C_{12}H_{11}{}^{81}BrNS^+$).

General Procedure for the Synthesis of Complexes 3a–c: Compound **2** was dissolved in dry CH_2Cl_2 or degassed DMSO and [Pd(dba)$_2$] or [Pd_2(dba)$_3$] was added. The mixture was stirred for 3 d. Subsequent addition of CH_2Cl_2 (10 mL) and Et_2O (90 mL) gave a precipitate, which was collected and washed twice by addition of CH_2Cl_2 and precipitation with Et_2O again. The precipitate was then dissolved in CH_2Cl_2 and filtered through Celite. After evaporation of the solvent, complexes **3a**–**c** were obtained as yellow powders.

Synthesis of 3a: Reaction of **2a** (1.22 g, 5.67 mmol) with [Pd(dba)$_2$] (3.26 g, 5.67 mmol) in CH_2Cl_2 (30 mL) afforded **3a** (1.74 g, 48%) after purification according to the general procedure. Analytically pure material was obtained by recrystallization from DMF/Et_2O. ^1H NMR (500 MHz, DMSO, 323 K): δ = 8.54 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, H^6_{pyr}), 7.40 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H^4_{pyr}), 6.96 (dd, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 5.9 Hz, 2 H, H^5_{pyr}), 4.13 (br. s, 4 H, CH_2), 2.80 (br. s, 12 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO, 323 K): δ = 179.4 (C-Pd), 151.3 (C^6_{pyr}), 143.9 (C^3_{pyr}), 129.8 (C^4_{pyr}), 118.7 (C^5_{pyr}), 70.1 (CH_2), 52.5 (CH_3) ppm. $C_{16}H_{22}Br_2N_4Pd_2$·H_2O (643.02): calcd. C 29.07, H 3.66, N 8.48; found C 29.01, H 4.00, N 8.84.

Synthesis of 3b: Reaction of **2b** (107 mg, 0.49 mmol) with [Pd_2(dba)$_3$] (222 mg, 0.24 mmol) in DMSO (5 mL) according to the general procedure gave **3b** (89 mg, 56%). An analytically pure sample was obtained by recrystallization from DMF/Et_2O. ^1H NMR (400 MHz, CD_2Cl_2, 253 K): δ = 8.67–8.62 (m, 2 H, H^6_{pyr}), 7.41 (m,

2 H, H^4_{pyr}), 6.94–6.90 (m, 2 H, H^5_{pyr}), 4.48 (dd, $^2J_{H,H}$ = 15.9, $^4J_{H,H}$ = 3.5 Hz, 1 H, low-field CH_2 of isomer A), 4.43 (dd, $^2J_{H,H}$ = 13.1, $^4J_{H,H}$ = 4.8 Hz, 1 H, low-field CH_2 of isomer B), 4.08 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, high-field CH_2 of isomer B), 3.52 (d, $^2J_{H,H}$ = 15.9 Hz, 1 H, high-field CH_2 of isomer A), 2.95, 2.94, 2.41, 2.40 (4× s, 6 H, CH_3 of isomers A and B) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO, 343 K): δ = 179.9 (C-Pd), 151.6 (C^6_{pyr}), 145.2 (C^3_{pyr}), 131.1 (C^4_{pyr}), 119.4 (C^5_{pyr}), 44.8 (CH_2), 22.3 (CH_3) ppm. $C_{14}H_{16}Br_2N_2Pd_2S_2$ (649.07): calcd. C 25.91, H 2.48, N 4.32; found C 26.17, H 2.67, N 4.03.

Synthesis of 3c: The reaction of **2c** (500 mg, 1.78 mmol) with [Pd_2(dba)$_3$] (797 mg, 0.87 mmol) in DMSO (10 mL) afforded **3c** as a precipitate. An additional crop of product was isolated from the combined supernatants of the precipitation process (total yield: 147 mg, 22%). ^1H NMR (500 MHz, DMSO, 323 K): δ = 8.49 (d, $^3J_{H,H}$ = 5.6 Hz, 2 H, H^6_{pyr}), 8.07 (d, $^3J_{H,H}$ = 7.4 Hz, 4 H, H_{Ph}), 7.46–7.38 (m, 8 H, 2H^4_{pyr} + 6H_{Ph}), 6.99 (dd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 5.6 Hz, 2 H, H^5_{pyr}), 5.03 (br. d, $^3J_{H,H}$ = 14.3 Hz, 2 H, CH_2), 4.17 (br. d, $^3J_{H,H}$ = 14.3 Hz, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO, 323 K): δ = 180.5 (C-Pd), 151.0 (C^6_{pyr}), 145.6 (C^3_{pyr}), 133.0 (C_{Ph}-H), 132.2 (C^4_{pyr}), 130.2 (C_{Ph}-H), 129.8 (C_{Ph}), 129.4 (C_{Ph}-H), 119.4 (C^5_{pyr}), 48.3 (CH_2) ppm. $C_{24}H_{20}Br_2N_2Pd_2S_2$ (773.21): calcd. C 37.28, H 2.61, N 3.62; found C 37.36, H 2.69, N 3.58.

Synthesis of 4a: Methanolic HBr (3.5 mL, 0.2 M in MeOH, 0.7 mmol) was added to **3a** (0.203 g, 0.31 mmol) dissolved in dry CH_2Cl_2 (30 mL). After 2 d, the precipitate formed was separated and the supernatant evaporated to dryness to give a yellow powder (0.205 g, 82%). Recrystallization from DMF/Et_2O afforded analytically pure material. ^1H NMR (500 MHz, DMSO, 323 K): δ = 13.14 (br. s, 1 H, NH), 8.35 (br. s, 1 H, H^6_{pyr}), 7.97 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, H^4_{pyr}), 7.53 (t, $^3J_{H,H}$ = 6.7 Hz, 1 H, H^5_{pyr}), 4.19 (s, 2 H, CH_2), 2.85 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO, 323 K): δ = 149.9 (C^3_{pyr}), 138.8 (C^6_{pyr}), 135.5 (C^4_{pyr}), 121.1 (C^5_{pyr}), 69.5 (CH_2), 52.0 (CH_3), C-Pd not resolved ppm. $C_8H_{12}Br_2N_2Pd\cdot 1/8$ DMF (402.42): calcd. C 24.44, H 3.15, N 7.23; found C 24.51, H 3.18, N 6.90.

Synthesis of 4b: Methanolic HBr (6 mL, 0.2 M in MeOH, 1.2 mmol) was added to **3b** (0.150 g, 0.23 mmol) in dry CH_2Cl_2 (30 mL). After 2 d, all volatiles were evaporated to give **4b** as a yellow powder, which was recrystallized from DMSO/Et_2O (0.138 g, 74%). ^1H NMR (500 MHz, DMSO): δ = 13.27 (br. s, 1 H, NH), 8.44 (pseudo t, $^3J_{H,H}$ = 5.8 Hz, 1 H, H^6_{pyr}), 8.10 (dd, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.0 Hz, 1 H, H^4_{pyr}), 7.55 (ddd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 1.1 Hz, 1 H, H^5_{pyr}), 4.43 (br. s, 2 H, CH_2), 2.72 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO): δ = 171.0 (C-Pd), 152.7 (C^3_{pyr}), 140.0 (C^6_{pyr}), 137.9 (C^4_{pyr}), 121.2 (C^5_{pyr}), 43.9 (CH_2), 23.4 (CH_3) ppm. $C_7H_9Br_2NPdS$ (405.45): calcd. C 20.74, H 2.24, N 3.45; found C 20.86, H 2.34, N 3.28.

Synthesis of 4c: Methanolic HBr (2 mL, 0.2 M in MeOH, 0.4 mmol) was added to **3c** (59 mg, 0.07 mmol) in dry CH_2Cl_2 (15 mL). The orange crystals which grew upon standing for 2 d were collected and dried in vacuo (40 mg, 56%). An analytically pure sample was obtained by recrystallization from DMF/Et_2O. ^1H NMR (500 MHz, DMSO, 323 K): δ = 13.33 (br. s, 1 H, NH), 8.45 (pseudo t, $^3J_{H,H}$ = 6.3 Hz, 1 H, H^6_{pyr}), 8.09 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^4_{pyr}), 7.82–7.78 (m, 2 H, H_{Ph}), 7.53 (dd, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 6.3 Hz, 1 H, H^5_{pyr}), 7.45–7.43 (m, 3 H, H_{Ph}), 4.78 (br. s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO, 323 K): δ = 171.4 (C-Pd), 152.5 (C^3_{pyr}), 139.8 (C^6_{pyr}), 137.4 (C^4_{pyr}), 131.4 (C_{Ph}), 130.6 (C_{Ph}-H), 129.7 (C_{Ph}-H), 129.4 (C_{Ph}-H), 121.0 (C^5_{pyr}), 46.1 (CH_2) ppm. $C_{12}H_{11}Br_2NPdS$ (467.52): calcd. C 30.83, H 2.37, N 3.00; found C 30.85, H 2.47, N 2.94.

Synthesis of 5c: [Me_3O]BF_4 (0.123 g, 0.83 mmol) was added to a solution of **2c** (0.193 g, 0.68 mmol) in MeCN and CH_2Cl_2 (1:1, 8 mL) and the mixture stirred for 14 h. All volatiles were evaporated and the residue was redissolved in MeCN (10 mL). After filtration through a short pad of SiO_2, volatiles were removed in vacuo to yield **5c** as an orange waxy solid (0.195 g, 74%). ^1H NMR (500 MHz, DMSO): δ = 9.12 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, H^6_{pyr}), 8.26 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H^4_{pyr}), 7.97 (dd, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 6.3 Hz, 1 H, H^5_{pyr}), 7.40–7.29 (m, 5 H, H_{ar}), 4.49 (s, 2 H, CH_2), 4.41 (s, 3 H, NCH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DMSO): δ = 147.6 (C^6_{pyr}), 145.1 (C^4_{pyr}), 141.6 (C-Br), 140.4 (C^3_{pyr}), 133.2 (C_{Ph}), 130.7 (C_{Ph}-H), 129.3 (C_{Ph}-H), 127.5 (C_{Ph}-H), 125.3 (C^5_{pyr}), 51.4 (NCH_3), 37.6 (CH_2) ppm. $C_{13}H_{13}BBrF_4NS$ (382.02): calcd. C 40.87, H 3.43, N 3.67; found C 40.88, H 3.43, N 3.75.

Methylation of 2b: A solution of **2b** (581 mg, 2.66 mmol) in CH_2Cl_2 and MeCN (1:2, 12 mL) was cooled to 0 °C. [Me_3O]BF_4 (392 mg, 2.65 mmol) was added and the solution was stirred at 0 °C for 15 min and at room temp. for 24 h. Evaporation of an aliquot indicated formation of a mixture of **2b** (9%), **5b** (45%), **6** (34%), and **7** (12%), according to ^1H NMR integration. Solvent evaporation and repetitive precipitation from acetone/hexane allowed for fractionation and gave pure batches of **2b** and **7**, while mixtures of **5b** and **6** failed to separate even upon crystallization; analytical data for these compounds were obtained from difference spectra.

5b: ^1H NMR (360 MHz, MeCN): δ = 8.76 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, H^6_{pyr}), 8.37 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, H^4_{pyr}), 7.92 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 5.9 Hz, 1 H, H^5_{pyr}), 4.37 (s, 3 H, NCH_3), 3.96 (s, 2 H, CH_2), 1.96 (s, 3 H, SCH_3) ppm. $C_8H_{11}BBrF_4NS$ (319.95): calcd. C 30.03, H 3.47, N 4.38; found C 30.04, H 3.42, N 4.40.

6: ^1H NMR (360 MHz, MeCN): δ = 8.50 (dd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^6_{pyr}), 8.11 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^4_{pyr}), 7.63 (dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 5.1 Hz, 1 H, H^5_{pyr}), 4.67 (s, 2 H, CH_2), 2.91 (s, 6 H, SCH_3) ppm. $C_8H_{11}BBrF_4NS$ (319.95): calcd. C 30.03, H 3.47, N 4.38; found C 30.04, H 3.42, N 4.40.

7: ^1H NMR (360 MHz, MeCN): δ = 8.93 (dd, $^3J_{H,H}$ = 6.3, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^6_{pyr}), 8.56 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.4 Hz, 1 H, 1H, H^4_{pyr}), 8.04 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 6.3 Hz, 1 H, H^5_{pyr}), 4.86 (s, 2 H, CH_2), 4.41 (s, 3 H, NCH_3), 2.96 (s, 6 H, SCH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, MeCN): δ = 144.5 (C-Br), 133.7 (C^3_{pyr}), 150.6 (C^6_{pyr}), 149.4 (C^4_{pyr}), 127.9 (C^5_{pyr}), 53.2 (CH_2), 47.0 (NCH_3), 25.8 (SCH_3) ppm. $C_9H_{14}B_2BrF_8NS$ (421.79): calcd. C 25.63, H 3.35, N 3.32; found C 25.70, H 3.44, N 3.44.

Synthesis of 8: Compound **5c** (0.195 g, 0.51 mmol) was dissolved in degassed DMSO (5 mL) and [Pd_2(dba)$_3$] (0.236 g, 0.26 mmol) was added. The mixture was stirred for 2 d, then LiBr (0.148 g, 1.7 mmol) was added and stirring was continued for another 4 h. CH_2Cl_2 (8 mL) was then added and the mixture filtered through Celite. Addition of Et_2O (90 mL) induced the formation of a yellow oil, which was separated by decantation and redissolved in MeOH (3 mL) and CH_2Cl_2 (5 mL). Reprecipitation with Et_2O (90 mL) yielded **8** as a yellow powder. Another crop of product was isolated from the combined supernatants upon standing. A powder slowly precipitated from the supernatant, which was washed with acetone and dried in vacuo (combined yield: 193 mg, 78%). ^1H NMR (500 MHz, DMSO, 298 K): δ = 8.60 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, H^6_{pyr}), 7.73 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, H^4_{pyr}), 7.34 (m, 3 H, 2H_{Ph} + H^5_{pyr}), 7.26 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{Ph}), 7.16 (m, 1 H, H_{Ph}), 5.02 (br. s, 2 H, CH_2), 4.74 (s, 3 H, NCH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ = 173.8 (C-Pd), 143.8 (C_{Ph}), 143.7 (C^6_{pyr}), 135.0 (C^4_{pyr}), 129.1 (C_{Ph}-H), 127.3 (C_{Ph}-H), 125.7 (C_{Ph}-H), 121.4 (C^5_{pyr}), 53.2 (NCH_3), 37.7 (CH_2) ppm; C^3_{pyr} not resolved. $C_{13}H_{13}Br_2NPdS$

Table 5. Crystallographic data for the reported structures.

	3a	3b	4a	4b	4c	8
Color, shape	yellow block	yellow plate	orange rod	yellow plate	yellow rod	yellow rod
Size [mm]	0.45×0.40×0.35	0.45×0.30×0.15	0.45×0.30×0.25	0.40×0.30×0.20	0.23×0.08×0.08	0.20×0.05×0.05
Empirical formula	$C_{16}H_{22}Br_2N_4Pd\cdot C_3H_7NO$	$C_{28}H_{32}Br_4N_4S_4Pd_4\cdot C_3H_7NO\cdot C_4H_{10}O$	$C_8H_{12}Br_2N_2Pd$	$C_7H_9Br_2NPdS$	$C_{12}H_{11}Br_2NPdS$	$C_{13}H_{13}Br_2NPdS$
Fw [g mol^{-1}]	716.09	1445.27	402.42	405.43	467.50	481.52
T [K]	193(2)	173(2)	173(2)	223(2)	223(2)	173(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)
a [Å]	9.1451(8)	8.6224(14)	8.8792(5)	14.2378(17)	9.4779(11)	13.8035(13)
b [Å]	32.397(3)	16.235(2)	12.1669(8)	6.5805(5)	13.3731(13)	11.5814(10)
c [Å]	8.8242(8)	17.138(3)	10.5364(6)	22.539(3)	10.7923(16)	8.9139(8)
α [°]	90	72.607(13)	90	90	90	90
β [°]	115.910(10)	88.346(13)	101.447(4)	92.210(14)	95.903(16)	90
γ [°]	90	84.824(13)	90	90	90	90
V [Å^3]	2351.6(4)	2280.0(6)	1115.63(12)	2110.1(4)	1360.7(3)	1425.0(2)
Z	4	2	4	8	4	4
D_{calc} [g cm^{-3}]	2.023	2.105	2.396	2.552	2.282	2.244
μ [mm^{-1}]	4.948	5.277	8.784	9.477	7.366	7.037
Total, unique refl.	16396, 4594	17284, 7874	21316, 3028	15548, 4081	10614, 2550	9916, 2544
R_{int}	0.0647	0.1031	0.0381	0.1100	0.0533	0.0722
Transmission range	0.218–0.294	0.184–0.315	0.655–0.697	0.064–0.156	0.543–0.556	0.345–0.393
Parameters, restraints	269, 0	465, 0	120, 0	147, 0	159, 1	104, 1
R,[a] Rw[b]	0.0348, 0.0803	0.0686, 0.1692	0.0238, 0.0492	0.0493, 0.1089	0.0263, 0.0452	0.0375, 0.0767
GOF	0.936	0.863	1.107	0.867	0.775	0.897
Largest hole, peak [e Å^{-3}]	–1.038, 0.859	–3.251, 2.332	–0.832, 0.440	–2.371, 1.708	–0.764, 0.502	–0.912, 1.156

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for all $I > 2\sigma(I)$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^4)]\}^{1/2}$.

(481.54): calcd. C 32.42, H 2.72, N 2.91; found C 32.25, H 2.83, N 2.95.

General Procedure for the Mizoroki–Heck Reaction: Bromoacetophenone (1 mmol), styrene (1.5 mmol), K_2CO_3 (1.1 mmol), and diethylene glycol dibutyl ether (0.25 mmol) as internal standard were dissolved in DMA (4.5 mL) and stirred at the reaction temperature for 10 min before adding a DMA solution of palladium complex (typically 0.2 μmol Pd in 0.5 mL). Aliquots were removed at given intervals, extracted with H_2O and hexane, and the organic layer was dried with Na_2SO_4 and the solvents evaporated. Conversions were determined by ^{1}H NMR spectroscopy ($CDCl_3$ solution) using substrate/standard integral ratios.

Solvento complexes were prepared as follows: the palladium complex was dissolved in MeCN, treated with $AgBF_4$ (2.0 mol equiv.), and stirred for 16 h protected from light. The formed precipitate was removed by filtration through Celite and the filtrate evaporated to leave the corresponding solvent complex, which was used without further purification.

Crystal Structure Determinations: Suitable single crystals were mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite monochromator. Data collection was performed using Mo-K_α radiation (λ = 0.71073 Å) with a nominal crystal-to-detector distance of 70 (for **3a**, **4b**, and **4c**), 100 (for **4a** and **8**), and 135 mm (for **3b**). All structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97.[27] The N-bound hydrogen atom in **4c** was located from a Fourier difference map and refined isotropically with a distance restraint [N–H 0.87(2) Å]. All other hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied to all structures using MULscanABS, as implemented in PLATON03.[28] Crystals of complex **3a** contained one molecule of DMF in the asymmetric unit, and **3b** cocrystallized with one molecule of DMF and one molecule of Et_2O. The absolute structure of **8** was confirmed by the pertinent Flack parameters [x = 0.02(2)]. Details of data collection and refinement parameters are collected in Table 5.

CCDC-711206 (for **3a**), -711207 (for **3b**), -711208 (for **4a**), -711209 (for **4b**), -711210 (for **4c**), -711211 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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